



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 216 109
A2

⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: 86111184.7

㉓ Int. Cl.4: D01F 6/62 , D01F 6/84 ,
D01D 4/02

㉒ Date of filing: 12.08.86

㉔ Priority: 23.08.85 JP 186429/85

㉕ Date of publication of application:
01.04.87 Bulletin 87/14

㉖ Designated Contracting States:
DE FR GB

㉗ Applicant: SUMITOMO CHEMICAL COMPANY,
LIMITED
15 Kitahama 5-chome Higashi-ku
Osaka-shi Osaka 541(JP)
Applicant: JAPAN EXLAN COMPANY, LTD.
2-8, Dojima-hama-2-chome Kita-ku
Osaka-shi Osaka 530(JP)

㉘ Inventor: Kobashi, Toshiyuki
1-6, Saldalikami-3-chome
Okayama-shi(JP)
Inventor: Takao, Seiji
781-3, Kanada
Okayama-shi(JP)
Inventor: Takagi, Jun
615-1, Kanaokanishimachi
Okayama-shi(JP)
Inventor: Sugimoto, Hiroaki
13-5, Kawanishicho-1-chome
Takatsuki-shi(JP)
Inventor: Hayatsu, Kazuo
11-8, Kamihozumi-2-chome
Ibaraki-shi(JP)

㉙ Representative: Henkel, Feller, Hänel &
Partner
Möhlstrasse 37
D-8000 München 80(DE)

A2

㉚ Polyester fiber.

EP 0 216 109

㉛ A polyester fiber of a large diameter having a tensile modulus of elasticity of 300 g/d or more can be obtained by melt-spinning a polyester which exhibits anisotropy in its molten state.

POLYESTER FIBER

FIELD OF THE INVENTION

This invention relates to a polyester fiber of high strength and high modulus of elasticity having a large diameter.

BACKGROUND OF THE INVENTION

There is eagerly awaited in the industrial world a thick fiber of high strength or high modulus of elasticity for such uses as the core of cable, rope, stringing, and wire substitutes.

When a metal wire is used as the thick fiber, it has the difficulty of causing noises or overcurrents in measuring instruments owing to its electroconductivity. When a composite material is used, there is the problem of insufficient adhesion at the interface between resin matrices and reinforcements. Further, when fine denier fibers are processed into rope, there occur the problems of much time and labor required in the processing steps and of abrasion during the processing.

There are also known as a typical thick synthetic fiber those of polyethylene terephthalate. However, their modulus of elasticity is not satisfactory, being about 25 to 150 g/d.

SUMMARY OF THE INVENTION

The object of this invention is to provide a synthetic fiber of a large diameter having high strength and high modulus of elasticity.

Thus, this invention relates to a polyester fiber obtained by melt-spinning an aromatic polyester which exhibits anisotropy in its molten state which fiber has a sectional area equivalent to that of a perfect circle with a diameter of 0.1 mm or more and a tensile modulus of elasticity of 300 g/d or more.

DETAILED DESCRIPTION OF THE INVENTION

The polyester which exhibits anisotropy in its molten state referred to in this invention means one which has a property of allowing the transmission of light at a temperature region in which it is flowable when the powder sample of the polyester is placed on a heating sample stage positioned between two polarizing plates crossed at an angle of 90° and the temperature of the sample is increased. Such polyesters are those formed of ar-

omatic dicarboxylic acids, aromatic diols and/or aromatic hydroxycarboxylic acid, and the derivatives thereof, disclosed in Japanese Patent Application Kokoku (Post-Exam. Publn.) Nos. I8016/81 and 20008/80, and optionally include copolymers of these with alicyclic dicarboxylic acids, alicyclic diols, aliphatic diols, and the derivatives thereof.

Examples of the aromatic dicarboxylic acids include terephthalic acid, isophthalic acid, 4,4'-dicarboxy diphenyl, 2,6-dicarboxynaphthalene, 1,2-bis(4-carboxyphenoxy)ethane; and the nuclear-substituted products thereof with an alkyl, aryl, alkoxy, or halogen group.

Examples of the aromatic diols include hydroquinone, resorcin, 4,4'-dihydroxydiphenyl, 4,4'-dihydroxybenzophenone, 4,4'-dihydroxydiphenylmethane, 4,4'-dihydroxydiphenylethane, 2,2-bis(4-hydroxyphenyl)-propane, 4,4'-dihydroxydiphenyl ether, 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxydiphenyl sulfide, 2,6-dihydroxynaphthalene, 1,5-dihydroxynaphthalene, and the nuclear-substituted products thereof with an alkyl, aryl, alkoxy, and halogen group.

Examples of the aromatic hydroxycarboxylic acids include p-hydroxybenzoic acid, m-hydroxybenzoic acid, 2-hydroxynaphthalene-6-carboxylic acid, 1-hydroxynaphthalene-5-carboxylic acid, and the nuclear-substituted products thereof with an alkyl, aryl, alkoxy, and halogen group.

Examples of alicyclic dicarboxylic acids include trans-1,4-dicarboxycyclohexane, cis-1,4-dicarboxycyclohexane and the substituted products thereof with an alkyl, aryl, and halogen group.

Examples of the alicyclic and aliphatic diols include trans-1,4-dihydroxycyclohexane, cis-1,4-dihydroxycyclohexane, ethylene glycol, 1,4-butanediol, and xylylene diol.

Among the combinations of the aforesaid materials, there may be mentioned as examples of a preferable aromatic polyester to be used in this invention:

(1) a copolyester comprising 40 to 70% by mole of p-hydroxybenzoic acid residue, 15 to 30% by mole of an above-mentioned aromatic dicarboxylic acid residue, and 15 to 30% by mole of an aromatic diol residue;

(2) a copolyester formed of terephthalic acid and/or isophthalic acid and chlorohydroquinone, phenylhydroquinone and/or hydroquinone; and

(3) a copolyester comprising 20 to 80% by mole of p-hydroxybenzoic acid residue and 20 to 80% by mole of 2-hydroxynaphthalene-6-carboxylic acid residue.

To attain the polyesters to be used in this invention by using these starting materials, they are subjected to polycondensation as they are or after esterified by an aliphatic or aromatic monocarboxylic acid or the derivative thereof, or an aliphatic alcohol, a phenol, or the derivative thereof.

The polycondensation can be carried out by using a known method including mass polymerization, solution polymerization and suspension polymerization. It may be conducted at 150 to 360°C under normal pressure or a reduced pressure of 10 to 0.1 Torr optionally in the presence of polymerization catalyst such as a Sb, Ti and Ge compound, a stabilizer such as a phosphorus compound, and fillers such as TiO_2 , $CaCO_3$, and talc, added thereto. The polymer thus obtained is heat-treated, as it is or in a pulverized form, in an inert gas or under reduced pressure to give a sample material for spinning. It can also be used after once granulated through an extruder.

It is considered that the aromatic polyester used in this invention should have a molecular weight range suitable for spinning. However, molecular weight cannot be used as a specification for aromatic polyester because often, depending on the composition and the structure of aromatic polyester, no solvent is found which can dissolve the polyester uniformly, so the molecular weight of the polyester cannot be determined accurately.

Accordingly, the present inventors have introduced a characteristic value termed "flow temperature" as a physical porperty corresponding to molecular weight. The "flow temperature" is defined as the temperature at which the aromatic polyester sample gives an apparent viscosity of 48,000 poises as the sample flows through a orifice having a diameter of 1 mm and a length of 10 mm at a pressure of 100 kg/cm² when the temperature of the sample is increased at a rate of 4°C/min by the use of a Flow Tester CFT-500 (a trade name, mfd. by Shimadzu Corp.).

The present inventors have synthesized aromatic polyesters of various compositions with varied flow temperatures, and found that aromatic polyesters having a flow temperature of 280 to 380°C are suitable for the purpose of this invention.

When the flow temperature of the polyester is lower than the above-mentioned temperature range, the polyester tends to undergo a reaction in the molten state or the elongation of the fiber obtained is unsatisfactory; whereas when it is higher than the range, since the processing (i.e. spinning) temperature becomes high, the polyester tends to undergo decomposition or crosslinking, and also the load applied to the spinning apparatus becomes too high.

As the apparatus for melt spinning in this invention, there may be used conventional extruders of a plunger type or a screw type. The spinning temperature is 280 to 420°C, preferably 300 to 400°C. Temperatures lower than the above-mentioned temperature range will result in too large load on the apparatus or not uniform melting of the sample, whereas temperatures higher than the range may cause the decomposition of the polymer.

For obtaining a fiber of a large diameter, which is one of the requisites in this invention, spinning is preferably carried out by the use of a spinneret having a hole diameter of 0.5 to 5 mm, more preferably 1 to 3 mm. The shear rate is preferably 100/sec to 1000/sec. Since polyesters which exhibit anisotropy in the molten state tend to be highly oriented by shear, the ratio of the land length to the diameter of the hole is preferably 0.5 or more, more preferably 1 or more; further, when a hole of a large diameter, for example 1 mm or more, is used, the ratio of the land length to the diameter of the hole to be used is preferably 3 or more.

As to the thickness of the fiber, its diameter - (calculated in terms of the diameter of a perfect circle having an equivalent sectional area, when the fiber has a modified cross section other than a perfect circle) must be 0.1 mm or more, preferably 0.3 mm or more.

The fiber, thus obtained shows excellent modulus of elasticity and strength as compared with thick fibers of conventional nylon and polyester.

The fibers obtained by spinning according to this invention are then taken up or drawn down as they are or after adhering a textile oil thereto. The velocity of taking up or drawing down is determined according to the thickness of the fiber to be obtained. The cross section of the fiber can be selected from various shapes including a circle, an ellipse, and a variety of irregular shapes. The production of fiber of such a cross section can be attained by using a spinneret having a discharge opening of various shapes such as

[●], [-], [λ], [+], [×] and [Λ].

Although the fiber thus obtained can be used as they are, their modulus of elasticity can be further increased by subjecting them to heat treatment, drawing, or combination of these.

Thus, the fiber of this invention is obtained.

The polyester fiber having a large diameter obtained by the method mentioned above has a high modulus of elasticity and, because of its large thickness, an excellent abrasion resistance.

The fiber obtained according to this invention can be used for rope, cables, FRP, F RTP, speaker cones, protective clothes, tension members, and other similar uses.

(Example)

This invention will be explained further in detail below with reference to Examples and Comparative Examples. However, they are merely for the sake of illustration and the invention is not limited thereto.

In the examples, the tensile test of the fiber was conducted by using an Autograph UM-500 (a trade name, mfd. by Toyo Baldwin Co., Ltd.) with a specimen gap of 50 mm and a stretching rate of 5 mm/min.

Optical anisotropy was examined by placing a sample on a heating stage and observing the sample with the naked eye under polarized light while increasing the temperature of the sample at a rate of 25°C/min.

Referential Example I

In a polymerization vessel having a comb-type stirrer, were placed 7.20 kg (40 moles) of p-acetoxibenzoic acid, 2.49 kg (15 moles) of terephthalic acid, 0.83 kg (5 moles) of isophthalic acid, and 5.45 kg (20.2 moles) of 4,4'-diacetoxypiphenyl, and the resulting mixture was brought to elevated temperature with stirring in a nitrogen gas atmosphere and polymerized at 330°C for 3 hours. During the period acetic acid formed was removed and the polymerization was carried out with powerful stirring. Thereafter, the reaction system was cooled gradually and the polymer formed was taken out at 200°C from the system. The yield of polymer was 10.88 kg, 97.8% of theoretical yield. The polymer was pulverized in a hammer mill to give particles of 2.5 mm or less. The polymer powder was then treated in a rotary kiln in nitrogen atmosphere at 280°C for 5 hours. The powder thus obtained had a "flow temperature" of 326°C and showed optical anisotropy at temperatures of 350°C or more.

Referential Example 2

A copolyester was synthesized from 2,5-diacetoxypiphenyl and terephthalic acid in the same manner as in Referential Example I. The polyester obtained had a "flow temperature" of 318°C and showed optical anisotropy at temperatures of 340°C or more.

Example I

The polyester obtained in Referential Example I was melt-spun by using a screw-type extruder of 30 mm diameter. The spinneret used had a hole diameter of 3 mm, a hole length of 36 mm, a number of holes of 1, and a discharge opening of a perfectly circular shape. The polyester was fed from a hopper and melt-spun at 365°C with varied output rates and take-up velocity. Stable spinning was conducted at various fiber diameters to give transparent, pale yellow fibers.

The fibers were annealed in nitrogen at 320°C for 3 hours. One of the fibers annealed was subjected to a tensile test. The other annealed fiber was subjected to a fatigue test and then to a tensile test. The fatigue test comprises winding the fiber five times around a stainless steel axle of 30 cm diameter and then rotating the axle for 5 minutes at a rate of 60 r.p.m. The results of these tensile tests are shown in Table I.

Comparative Example I

Polyethylene terephthalate RT-580 (a trade name, mfd. by Toyobo Co., Ltd.) was used to spin a fiber at 300°C in the same manner as in Example I except for the following procedures. The extruded fiber was quenched by introducing it into water at a point 5 cm below the spinneret. The quenched fiber was further stretched 4-fold at 150°C and then annealed under tension at 185°C for 3 hours. The results of the tensile test of the annealed fiber and the tensile test of the fiber after fatigue test are shown in Table I.

Example 2

The polyester obtained in Referential Example 2 was used to spin a fiber at 360°C in the same manner as in Example I. A transparent, pale yellow fiber was obtained. The fiber was annealed in nitrogen at 320°C for 3 hours to give a fiber having the properties shown in Table 2.

Table 1 Results of tensile test of annealed fiber

	Fiber diameter (mm)	Tensile test			Tensile test (after fatigue test)	
		Strength (g/d)	Elongation (%)	Modulus of elasticity (g/d)	Strength (g/d)	Elongation (%)
Example 1	0.72	4.7	1.2	487	4.3	1.0
	0.51	5.8	1.7	509	5.3	1.6
	0.37	8.2	1.9	582	7.4	1.6
Comparative Example 1	0.52	2.4	>100	30	2.1	>100
						27

Table 2 Result of tensile test of annealed fiber

	Fiber diameter (mm)	Strength (g/d)	Elongation (%)	Modulus of elasticity (g/d)
Example 2	0.61	4.3	1.3	370
	0.42	5.9	1.5	462

Claims

I. A polyester fiber obtained by melt-spinning an aromatic polyester which exhibits anisotropy in its molten state which fiber has a sectional area equivalent to that of a perfect circle with a diameter of 0.1 mm or more and a tensile modulus of elasticity of 300 g/d or more.

2. A polyester fiber according to Claim 1, which is obtained by melt-spinning a polyester which exhibits anisotropy in its molten state by using a spinneret having a hole diameter of 0.5 to 5 mm and a ratio of land length to hole diameter of 0.5 or more at a shear rate of 100 to 1000/sec.

20

25

3. A polyester fiber according to Claim 1 or 2, wherein the polyester which exhibits anisotropy in its molten state has a flow temperature of 280 to 380°C.

30

35

40

45

50

55